

ACID-CATALYZED ALCOHOLYSIS OF METAL-METAL BONDS OF ORGANOSILYL- AND ORGANOGERMYL-SUBSTITUTED FERROCENES

MAKOTO KUMADA, TADAO KONDO, KOJI MIMURA, KEIJI YAMAMOTO and MITSUO ISHIKAWA

Department of Synthetic Chemistry, Kyoto University, Kyoto 606 (Japan)

(Received April 6th, 1972)

SUMMARY

Acid-catalyzed alcoholysis of thirteen ferrocenes bearing M-M (M = Si and/or Ge) substituents has been studied under ambient conditions. With a low concentration of hydrogen chloride ($\sim 0.053 M$) no significant protodemetalation to give ferrocene occurred, while the M-M bond underwent alcoholysis smoothly to form in most cases a 1,3-diferrocenyl- or a 1,1'-ferrocenylenedisiloxane (or digermoxane), depending on the structure of the starting compound. A ferricenium ion intermediate having the M-M grouping is postulated in the light of the fact that the presence of both oxygen and an acid is essential for the occurrence of the reaction in alcohol.

INTRODUCTION

There is ample evidence to show that protodesilylation of certain trialkylsilyl-substituted ferrocenes¹⁻³ follows a similar path to that in the benzene series, the latter being typical of electrophilic substitution reactions⁴.

In our previous communication⁵, we reported that although ferrocenes containing the Si-Si groupings as substituents similarly undergo protodesilylation in refluxing methanolic solution of hydrogen chloride, another type of reaction which results in a selective cleavage of the silicon-silicon linkage adjacent to the ferrocenyl group becomes significant when the acid catalyst concentration is less than $0.015 M$. At a much lower hydrogen chloride concentration the protodesilylation is almost suppressed, while the unusually easy cleavage of the silicon-silicon bond is still observed. Thus our primary concern has been to obtain some insight into the mechanism of the latter reaction. This paper describes acid-catalyzed alcoholysis of several ferrocene derivatives which contain the M-M (M = Si and/or Ge) groupings under ambient conditions, and a possible effect of oxygen present in the reaction mixture on the course of reaction.

RESULTS AND DISCUSSION

Preparative methods, some physical properties for ferrocene derivatives (I)-(XI) used in the present study are reported in the preceding paper⁶. The hydrogen

TABLE I

ALCOHOLYSIS OF ORGANOSILYL- AND ORGANOGERMYL-SUBSTITUTED FERROCENES IN THE PRESENCE OF HYDROGEN CHLORIDE

Compound ^a	Reaction conditions			Temp.	Time (h) ^b	Products ^c (yield) ^d (%)
	(mmol)	Alcohol (ml)	[HCl] (mM)			
(I)	(11.4)	EtOH(180)	1.1	^d	1	(XII)(37), ferrocene (2.1)
(I)	(0.633)	MeOH(9)	1.2	^d	2.5	(XIII)(85.0 ^e), ferrocene (5.9 ^e)
(I)	(1.20)	EtOH(10)	18	^f	31	(XIII)(50.2 ^e), (XIV)(43.0 ^e), ferrocene (6.8 ^e)
(II)	(0.131)	EtOH(5)	11	^f	290	(XII)(48.0)
(III)	(1.01)	EtOH(5)	11	^f	280	(XV)(18.6)
(IV)	(0.987)	EtOH(8)	26	^f	5.5	(XV)(41.6)
(V)	(0.100)	EtOH(1)	53	^f	7	(XVI)(100 ^e)
(V)	(0.449)	MeOH(10)	2.4	^d	2.5	(XVI)(95.0 ^e), ferrocene (4.4 ^e)
(V)	(5.59)	EtOH(40)	15	^f	8	(XVI)(21.4 ^e), (XVIII)(32.5 ^e), (XIX)(15.3 ^e)
(VI)	(0.100)	EtOH(1)	53	^f	13	(XVI)(97.2 ^e)
(VII)	(0.100)	EtOH(1)	53	^f	27	(XVI)(99.4 ^e)
(VII)	(0.946)	EtOH(20)	53	^f	47	(XVI)(5.5), (XX)(18.8)
(VIII)	(0.100)	EtOH(1)	53	^f	1	(XVII)(90.7 ^e)
(IX)	(0.100)	EtOH(1)	53	^f	5	(XVII)(99.0 ^e)
(X)	(0.100)	EtOH(1)	53	^f	0.4	(XVI)(100 ^e)
(XI)	(0.100)	EtOH(1)	53	^f	0.8	(XVII)(91.3 ^e)
(XVII)	(0.100)	EtOH(1)	53	^f	3	(XVII)(97.2 ^e)
(XIX)	(0.100)	EtOH(1)	53	^f	4	(XVI)(76.5 ^e)

^a (I) (Pentamethyldisilyl)ferrocene; (II) [(trimethylgermyl)dimethylsilyl]ferrocene; (III) [(trimethylsilyl)dimethylgermyl]ferrocene; (IV) (pentamethyldigermanyl)ferrocene; (V) 1,1'-bis(pentamethyldisilyl)ferrocene; (VI) 1,1'-bis(heptamethyltrisilyl)ferrocene; (VII) 1,1'-bis(trimethylgermyl)dimethylsilyl]ferrocene; (VIII) 1,1'-bis[(trimethylsilyl)dimethylgermyl]ferrocene; (IX) 1,1'-bis(pentamethyldigermanyl)ferrocene; (X) 1,2-(1,1'-ferrocenylene)tetramethyldisilane; (XI) 1,2-(1,1'-ferrocenylene)tetramethyldigermane; (XII) (ethoxydimethylsilyl)ferrocene; (XIII) (methoxydimethylsilyl)ferrocene; (XIV) (pentamethyldisiloxy)ferrocene; (XV) 1,3-diferrocenyltetramethyldigermoxane; (XVI) 1,3-(1,1'-ferrocenylene)tetramethyldisiloxane; (XVII) 1,3-(1,1'-ferrocenylene)tetramethyldigermoxane; (XVIII) 1-(ethoxydimethylsilyl)-1'-(pentamethyldisilyl)ferrocene; (XIX) 1-(pentamethyldisiloxy)-1'-(pentamethyldisilyl)ferrocene; (XX) 1-(ethoxydimethylsilyl)-1'-(trimethylgermyl)dimethylsilyl]ferrocene. ^b Required for approximate completion of the reaction. ^c Isolated yield unless otherwise noted. ^d At reflux temperature of the reaction mixture. ^e Determined by GLC analysis. ^f At room temperature.

TABLE 2

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR NEW COMPOUNDS

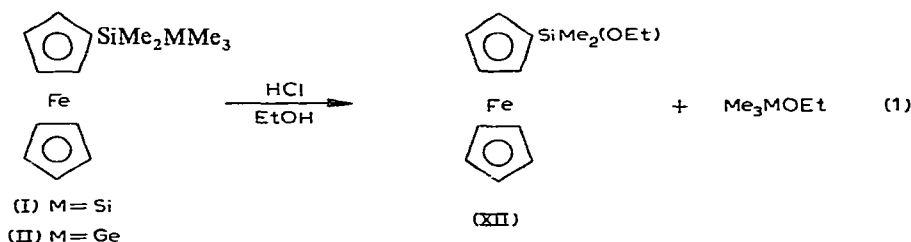
Compound		M.p. (°C)	Analysis found (calcd.) (%)	
No.	Formula		C	H
(XII)	C ₁₄ H ₂₀ FeOSi ^a		57.95 (58.34)	6.98 (6.99)
(XV)	C ₂₄ H ₃₀ Fe ₂ Ge ₂ O	117.5–118.5	48.81 (48.74)	5.31 (5.11)
(XVII)	C ₁₄ H ₂₀ FeGe ₂ O	91.5–92.5	41.91 (41.49)	5.23 (4.97)
(XIX)	C ₂₀ H ₃₈ FeOSi ₄		52.56 (51.92)	8.46 (8.28)
(XX)	C ₁₉ H ₃₄ FeGeOSi ₂		49.90 (49.28)	7.66 (7.40)

^a n_D²⁰ 1.5580.

chloride concentration ranged over 0.001–0.053 M. Most of the reactions were conducted at room temperature. Under these conditions, any protodemetalation to give ferrocene was found to be insignificant, but cleavage of M–M bonds adjacent to the ferrocenyl group took place smoothly. The extent of the reaction was readily followed by GLC. All results including the reaction conditions employed are summarized in Table 1. The reaction products were isolated by distillation and/or recrystallization. Their physical properties and analytical data are listed in Table 2, and ¹H NMR data in Table 3.

Cleavage of monosubstituted ferrocenes

Both (pentamethyldisilanyl)ferrocene (I) and [(trimethylgermyl)dimethylsilyl]ferrocene (II) have been found to undergo cleavage of the Si–M (M=Si or Ge) bond in an ethanolic solution of hydrogen chloride at room temperature to give (ethoxydimethylsilyl)ferrocene (XII). Qualitatively, (I) reacted much faster than (II). (Methoxydimethylsilyl)ferrocene (XIII) was similarly obtained in good yield from



(I) with methanol as solvent. (Pentamethyldisiloxanyl)ferrocene (XIV) found in one case may be a secondary condensation product formed from (XII) and ethoxytrimethylsilane formed during the reaction, presumably because of the prolonged period of reaction time.

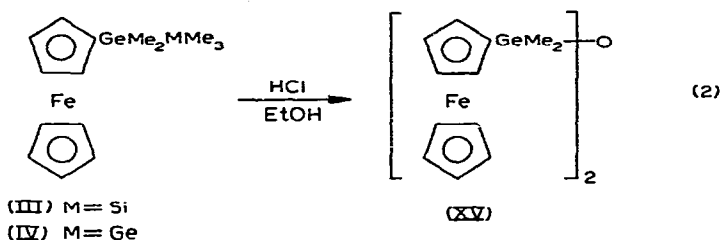
On the other hand, the cleavage of [(trimethylsilyl)dimethylgermyl]ferrocene (III) and of (pentamethyldigermanyl)ferrocene (IV) in ethanol containing hydrogen

TABLE 3
¹H NMR DATA FOR NEW COMPOUNDS

Compound	Formula	Chemical shifts ^{a,b}						
		H _a	H _b	H _c	H _d	H _e	H _f	H _f
(XII)	C ₃ H ₄ ^a FeC ₃ H ₄ Si(CH ₃) ₂ OCH ₃ CH ₃ ^b	9.70 (s)	8.84 (t)	6.41 (q)	5.98 (s)	5.87 (A ₂ B ₂)		
(XV)	[C ₃ H ₃ ^b FeC ₃ H ₃ Ge(CH ₃) ₂] ₂ O	9.58 (s)	6.03 (s)	5.95 ^d (A ₂ B ₂)				
(XVII)	Fe[C ₃ H ₂ ^b Ge(CH ₃) ₂] ₂ O	9.51 (s)	5.86 (A ₂ B ₂)					
(XIX)	(CH ₃) ₃ SiSi(CH ₃) ₂ C ₃ H ₃ FeC ₃ H ₄ Si(CH ₃) ₂ OSi(CH ₃) ₃	9.81 ^c (s)	9.77 ^c (s)	9.55 ^c (s)	9.51 ^c (s)	5.81 ^c (A ₂ B ₂)	5.60 ^c (A ₂ B ₂)	
(XX)	(CH ₃) ₃ GeSi(CH ₃) ₂ C ₃ H ₄ FeC ₃ H ₄ Si(CH ₃) ₂ OCH ₃ CH ₃ ^b	9.61 ^c (s)	9.49 ^c (bs)	8.74 ^c (t)	6.25 ^c (q)	5.80 ^c (A ₂ B ₂)	5.61 ^c (A ₂ B ₂)	

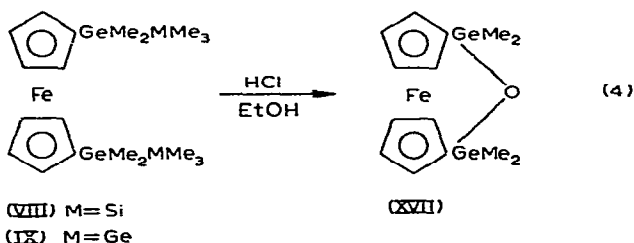
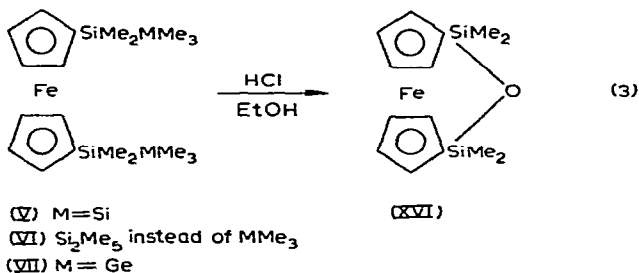
^a Determined in carbon tetrachloride solution with cyclohexane as an internal standard and the data are given in τ-values. ^b s, singlet; bs, broad singlet; t, triplet; and q, quartet. ^c Determined in benzene solution with benzene as an internal standard. ^d One of the A₂B₂ absorptions was overlapped with absorption H_b.

chloride gave rise to an unexpected product, 1,3-diferrocenyltetramethyldigermoxane (XV). Here again, a marked difference in reactivity between (III) and (IV) was observed, which will be discussed in detail in a forthcoming paper.



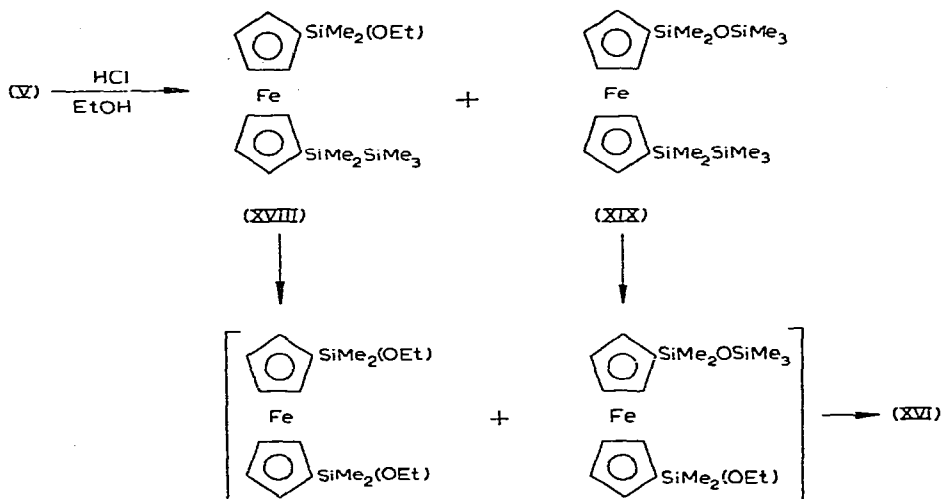
Cleavage of disubstituted ferrocenes

The reaction of 1,1'-disubstituted ferrocenes (V)–(IX) always resulted finally in the formation of those products in which the two cyclopentadienyl rings are intramolecularly bridged by a metaloxane bond such as 1,3-(1,1'-ferrocenylene)tetramethyldisiloxane (XVI) and -digermoxane (XVII) [eqns. (3) and (4)].



The possible intermediates, 1-(ethoxydimethylsilyl)-1'-(pentamethyldisilanyl)ferrocene (XVIII) and 1-(pentamethyldisiloxanyl)-1'-(pentamethyldisilanyl)ferrocene (XIX) were in fact detected, along with (XVI), by GLC analysis in the early stages of the reaction of (V). These compounds were isolated pure by preparative GLC, and separately allowed to react under the same conditions as above, giving (XVI). Other conceivable products, *e.g.*, 1,1'-bis(ethoxydimethylsilyl)ferrocene⁷ or 1,1'-bis(pentamethyldisiloxanyl)ferrocene⁸, could not be detected in the present experiments. However, it was confirmed that these two compounds readily undergo condensation in the presence of acid to afford (XVI).

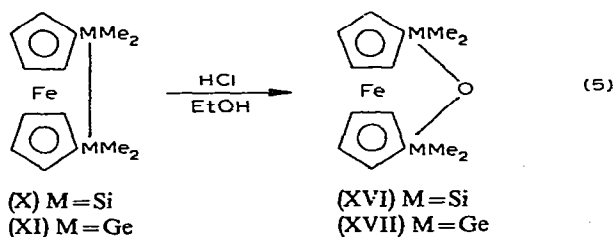
Summarizing these results, the cleavage of (V) is apparently stepwise in nature and can be best represented by the following scheme:



1-(Ethoxydimethylsilyl)-1'-[(trimethylgermyl)dimethylsilyl]ferrocene, (XX), is formed analogously as the initial product from (VII), but more slowly than is (XVIII) from (V). This is in good accord with the fact that the cleavage of the Si-Si bond in compound (I) occurs qualitatively much faster than that of the Si-Ge bond in (II), as described above.

Cleavage of bridged ferrocenes

Bridged ferrocenes, 1,2-(1,1'-ferrocenylene)tetramethyldisilane (X) and -digermane (XI), undergo cleavage with much greater ease under the standard conditions (see Table 1) to give (XVI) and (XVII), respectively. The observed high reactivity of bridged ferrocenes, (X) and (XI), toward the acid-catalyzed alcoholysis of M-M linkages might be ascribed in part to the internal strain of the bridging, though their NMR spectral data are not consistent with any occurrence of the type of ring tilting which has been observed with the carbon congeners of (X) and (XI)⁹.



The effect of hydrogen chloride and oxygen on the cleavage reaction

As described in the earlier communication⁵, the lower the concentration of hydrogen chloride in methanol, the higher becomes the apparent yield in a selective cleavage of the silicon-silicon bond adjacent to the ferrocenyl group, *e.g.*, in (penta-methyldisilanyl)ferrocene (I). However, this merely means that the rate of protodesilylation of both (I) and the (methoxydimethylsilyl)ferrocene (XIII) formed as a primary product, is reduced; the latter compound was, indeed, shown to survive

under the conditions employed. Thus, in general, we found that the protodemetalation was negligible when the concentration of hydrogen chloride was less than 0.005 *M* at reflux of solvent or 0.050 *M* at room temperature, and therefore acid-catalyzed alcoholysis of the M–M (M = Si and/or Ge) bond of compounds (I)–(XI) could be conveniently examined.

In addition, the most interesting feature of the reaction has emerged from the following findings: (I) is substantially inert either in an oxygen-free ethanolic solution of hydrogen chloride (0.053 *M*) (except for very slow protodesilylation to give ferrocene) or in acid-free ethanol under ambient conditions.

It is well known that ferrocene is easily autoxidized in an acidic medium to form ferricenium ion¹⁰, which decomposes rapidly in neutral or basic solutions, to give partly ferrocene along with hydroxides of iron^{11,12}. Therefore, the fact that the presence of both oxygen and an acid in alcohol is essential for the present cleavage reaction may be best interpreted by postulating that ferricenium ion intermediates having M–M (M = Si and/or Ge) groupings are involved in the course of the reaction. The M–M bond is much more polarizable¹³, and hence reactive, than the carbon–carbon bond. The well-established strongly electron-withdrawing nature of the ferricenium group¹⁴ will facilitate the alcoholysis of the M–M bond by making the group with ferricenium having the M system in the α -position a good leaving group. It should be noted that a similar type of alcoholysis of the M–M (M = Si or Ge) bond in alkenyldisilanes and -digermanes is also observed in the presence of palladium(II) complexes^{15,16}.

Convincing evidence for the intervention of ferricenium ions in the course of the reaction will be presented in the succeeding paper.

EXPERIMENTAL

Alcoholysis of organosilyl- and organogermyl-substituted ferrocenes in the presence of hydrogen chloride

The following is typical of the procedures used. A solution of 380 mg (1.20 mmol) of (pentamethyldisilanyl)ferrocene (I) in 10 ml of absolute ethanol containing hydrogen chloride (0.018 *M*) was allowed to stand at room temperature for 31 h. The solution was then added to water (50 ml) and the mixture was extracted twice with 30 ml portions of petroleum ether. The extracts were combined, dried over sodium sulfate and concentrated. GLC analysis (30% Apiezon L on Celite, at 270°) of the concentrate showed it to consist of (ethoxydimethylsilyl)ferrocene (XII) (50.2%), (pentamethyldisiloxanyl)ferrocene (XIV) (43.0%), and ferrocene (6.8%). Although (XIV) could not be separated completely pure because of the proximity of its position on GLC to that of (XII), it was identified by comparison of the GLC retention time and IR and NMR spectra of a sample in the impure state with those for an authentic sample. (XII) was isolated by preparative GLC in another run and identified by elemental analysis, IR and NMR spectra. The IR spectra of both (XII) and (XIV) exhibit bands near 1104 and 1000 cm^{-1} characteristic of an unsubstituted cyclopentadiene ring and in addition (XII) has bands near 1165 and 945 cm^{-1} characteristic of the ethoxysilane, while (XIV) has bands in the region of 1070–1100 cm^{-1} due to $\nu(\text{Si-O})$.

All results together with conditions under which reactions of compounds

(I)–(XI), (XVIII), and (XIX) were carried out are summarized in Table 1. Some physical properties and analytical data for the new compounds are listed in Table 2 and their ^1H NMR data in Table 3.

Attempted reaction of (I) in degassed ethanolic solution of hydrogen chloride

In a glass ampoule was placed a solution of 123 mg (0.388 mmol) of (I) in 10 ml of absolute ethanol containing hydrogen chloride (0.053 M). The mixture was degassed by repeated freezing and melting under vacuum. The ampoule was sealed and allowed to stand at room temperature for 308 h. It was then opened, and half of the reaction mixture was worked up as described above and shown by GLC to consist of unchanged (I) (93.3% yield) and a trace of ferrocene. It was ascertained that hydrogen chloride had not been completely removed by degassing. The remaining half of the reaction mixture was allowed to stand for some hours with occasional shaking, and then transferred into a glass ampoule. After 142 h at room temperature, the reaction mixture was found to contain the starting material (I) (53.5%), (XII) (40.0%), and traces of ferrocene.

Attempted reaction of (I) with oxygen in ethanol

(I) (122 mg, 0.385 mmol) was dissolved in 30 ml of dry ethanol. Dry oxygen was bubbled into the solution at room temperature for 120 h. After evaporation of the solvent, the residue was chromatographed on alumina to give 106 mg (87.3% yield) of unchanged (I).

REFERENCES

- 1 R. A. Benkeser, Y. Nagai and J. Hooz, *J. Amer. Chem. Soc.*, 86 (1964) 3742.
- 2 G. Marr and D. E. Webster, *J. Organometal. Chem.*, 2 (1964) 99.
- 3 G. Marr and D. E. Webster, *J. Chem. Soc. B*, (1968) 202.
- 4 C. Eaborn and R. W. Bott, in A. G. MacDiarmid (Ed.), *Organometallic Compounds of the Group IV Elements*, Vol. 1, Part 1, Dekker, New York, 1968, p 407.
- 5 M. Kumada, K. Mimura, M. Ishikawa and K. Shiina, *Tetrahedron Lett.*, (1965) 83.
- 6 M. Kumada, T. Kondo, K. Mimura, M. Ishikawa, K. Yamamoto, S. Ikeda and M. Kondo, *J. Organometal. Chem.*, 43 (1972) 293.
- 7 R. L. Shaaf, P. T. Kan and C. T. Lenk, *J. Org. Chem.*, 26 (1961) 1790.
- 8 R. L. Shaaf, P. T. Kan and C. T. Lenk, *J. Org. Chem.*, 25 (1960) 1986.
- 9 Ref. 6 in T. H. Barr and W. E. Watts, *Tetrahedron*, 24 (1968) 6111.
- 10 G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *J. Amer. Chem. Soc.*, 74 (1952) 2125.
- 11 R. M. Golding and L. E. Ogel, *J. Chem. Soc.*, (1962) 363.
- 12 T. D. Smith, *J. Chem. Soc.*, (1961) 473.
- 13 A. I. Vogel, W. T. Cresswell and J. Leicester, *J. Phys. Chem.*, 58 (1954) 174.
- 14 S. P. Gubin and A. A. Lubovich, *J. Organometal. Chem.*, 22 (1970) 183.
- 15 K. Yamamoto, M. Kumada, I. Nakajima, K. Maeda and N. Imaki, *J. Organometal. Chem.*, 13 (1968) 329.
- 16 K. Yamamoto and M. Kumada, *J. Organometal. Chem.*, 35 (1972) 297.

J. Organometal. Chem., 43 (1972)